Chemical Studies of the Western Pacific Ocean. I. The Chemical Composition of the Oceanic Salt. Part 1.

By Yasuo MIYAKE.

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Under the guidance of Prof. Okada, Director of the Central Meteorological Observatory of Japan, a thorough investigation of the Western Pacific Ocean is now being contemplated. The present author, being charged with the chemical survey in this project, intends to determine first the chemical composition of the sea salt, precision in analyses being esteemed above all. The present paper records the results of the chemical analyses of the sea salt.

Today, we have a large number of reliable determinations[1] of the chemical composition of oceanic salt, among which W. Dittmar's seventy-seven analyses of samples of water collected from various localities and depths in the memorial "Challenger"-Expedition, are still highly regarded for their exactness. We can easily see in these numerous analyses that there is an astonishing close agreement among them. However, contemporary geochemistry is not satisfied with such mere agreement, and requires the delicate differences between them to the accuracy of the second order. In such minute differences, we have a possibility of perceiving the true sources and cycles of the elements occurring in the sea which are quite obscure even at the present time. In spite of numerous active chemical investigations in oceanography, these being mainly in the domains of fishery and chemical industry, accurate chemical analysis of waters from the Pacific Ocean near Japan has not yet been made from the stand point of exact analytical chemistry.

Samples of Sea Water. The dates and positions of collection are shown in Table 1.

Table 1.

No.	Date	Position		No.	Date	Position	
		Lat. N	Long. E			Lat. N	Long. E
31	Oct. 10, 1937.	24°53′	125°53′	61	Dec. 1, 1937	27°23′	136°48′
32	,, 10, ,,	25°25′	126°48′	62	,, 2, ,,	25°46′	137°17′
36	,, 11, ,,	27°25′	129°45′	64	,, ,, ,,	24°42′	137°50′
38	,, 12, ,,	29°12′	131°53′	67	,, ,, ,,	24°36′	139°27′
40	,, ,, ,,	30°28′	133°32′	70	,, 4, ,,	25°02′	141°30′
42	,, ,, ,,	31°13′	134°29′	73	,, 8, ,,	27°32′	141°58′
45	,, 13, ,,	33°05′	137°01′	75	,, 9, ,,	29°38′	140°56′
56	Nov. 30, ,,	32°40′	137°50′	76	,, ,, ,,	30°09′	140°40′
57	Dec. 1, ,,	30°04′	136°40′	81	,, 10, ,,	33°08′	139°49′

(1) F.W. Clarke, "The Data of Geochemistry," 126, Washington (1924).

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Methods of Analysis. The analytical procedures adopted will be briefly described in the following paragraphs.

(1) *Chlorinity.* The chloride determination of sea water is one of the most important problems in oceanographical research. The analytical method which is now internationally accepted, is M. Knudsen's system, in which Mohr's argentometry is adopted as a chemical procedure. We can determine the chloride content of sea water very easily, by Knudsen's volumetrical apparatus, the normal sea water supplied from his laboratory, and his hydrographical tables. However, this system has a very serious weakness in its analytical procedure. Mohr's argentometry needs much improvement from the stand point of today's analytical chemistry.[2]

There are two large sources of errors in this method of titration, one is due to the strong colloidal nature of the silver chloride precipitate, and the sign of this error tends to be minus while the other is a plus one which comes from the sensibility of the indicator. The latter is always about 0.15%, if the titration is done under a careful control, although it has no effect on the determination of chloride of sea water. On the other hand, the former is always larger and more serious, because its magnitude varies with the analytical conditions, i.e. the concentration of the solution, the rate of stirring, the velocity of the titration, etc. To obtain good results, one must stir the solution just enough during the titration, and one must not cease stirring before ascertaining that the red colour indicating the end point will not disappear again.

Fluorescein or its sodium salt uranin, for which we are indebted to K. Fajans and his collaborator, is a superior adsorption indicator for the chloride determination. Kolthoff[3] and Böttiger[4] stated that the argentometric titration with this indicator is very accurate when compared with the potentiometric titration. The present author has also verified the superiority of this indicator. He has contrived to use this dyestuff for the chloride determination of sea water, and obtained very satisfactory results. The indicator used is a mixture of 5 c.c. of 0.1% uranin solution and 100 c.c. of 1% starch solution, the starch serving as a protective colloid; and 2 c.c. of this indicator is added to each 15 c.c. of sea water.

Although the new indicator is used instead of potassium chromate, it is not at all necessary to change any other procedure of Knudsen's system. At any rate it is important that this improvement makes the best use of his hydrographical tables and his volumetric apparatus. The mean error of the titration with this new indicator is always under 0.015%, and the time needed for each titration is shorter than one half of that required for Mohr's method. Since the colour change at the end point is quite clear, and owing to the protective colloid, there is no danger of under titration caused by the too early appearance of the end point.

Burettes and pipettes, made according to Knudsen's type by Fujiwara Brothers and Co., were accurately calibrated.

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(2) Lottermoser and Lorenz, *Kolloid-Z.*, **68** (1934), 201.
(3) I.M. Kolthoff and L.H. van Berk, *Z. anal. Chem.*, **70** (1927), 369.
(4) W. Böttiger and K.O. Schmidt, *Z. anorg. allgem. Chem.*, **137** (1924), 246.

(2) *Sodium and potassium.* A 30 c.c. sample of sea water was taken with a pipette; the sulphate ion was removed in the present of acid with a solution of barium chloride; and the excess of barium chloride with calcium and magnesium was completely precipitated as carbonates and filtered off. After weighing the total chlorides of alkalies as usual, potassium was determined in the form of potassium chloroplatinate.

(3) *Calcium and magnesium.* A 100 c.c. portion of sea water was taken. First, after adding ammonium chloride containing a little ammonia, calcium oxalate was precipitated by boiling with ammonium oxalate. The precipitation was repeated two or three times in order to remove the occluded magnesium as much as possible. Calcium oxalate was filtered off; the precipitation was repeated. Finally it was ignited to calcium oxide. Weighing was done with due care of its hygroscopic nature.

Magnesium was determined with the filtrate from the calcium determination by the magnesium ammonium phosphate method: the precipitation was repeated and then ignited to magnesium pyrophosphate.

(4) *Sulphate.* A 30 c.c. sample was taken; a little hydrochloric acid was added; and the sulphate ion was precipitated by boiling with barium chloride. The precipitate of barium sulphate was allowed to settle down by standing for several hours and was then filtered through the finest filter (Swedish filtering paper No. 00). It was thoroughly washed with hot water until no chloride ion was detectable in the filtrate and then ignited to a constant weight.

(5) *Carbonate.* Although we could obtain undoubtedly a more accurate result by the back titration method for the determination of total carbonate ion in sea water than by direct titration, the latter method was used. A 100 c.c. portion of sea water was titrated with a standard hydrochloric acid solution with methyl orange as the indicator.

(6) *Bromine.* The determinations of this element with several gravimetric methods were tried many times without success owing to the small amount of free chlorine usually produced together with bromine, the values being apt to be too high. The colorimetric method (the method of W. J. Dibdin and L. H. Cooper[5]) was finally successful, which, however, is not so accurate as the gravimetric method.

(7) *Strontium and boron.* Strontium and boron in sea water were also determined. The details of the results will be published in the following paper.

The Results of the Analyses. Table 2 shows the results of the analyses, in which each element is expressed in number of grams per kilogram of sea water. Strontium is included in the weight of calcium. Likewise, only the chlorinity is mentioned here instead of chlorine and bromine.

The Composition of the Sea Salt from the Western Pacific. The percentage composition of oceanic salt, which has been computed from the data of total analysis mentioned above, is shown in Table 3. We can see

(5) F.D. Snell and C.T. Snell. "Colorimetric Methods of Analysis," 544, New York (1936).

that a very similar result has been obtained in each analysis, regardless of the position of securing the sample. This agreement seems to indicate a homogeneity in the composition of the sea salt of the Western Pacific Ocean.

Table 2.

No.	Chlorinity	SO_4	CO_3	Ca	Mg	Na	K
31	19.29	2.6973	0.0710	0.4276	1.3023	10.5795	0.3787
32	19.27	2.6893	0.0698	0.4295	1.2967	10.6457	0.3693
36	19.22	2.6734	0.0710	0.4253	1.2978	10.5937	0.3663
38	19.17	2.6790	0.0701	0.4234	1.2989	10.5018	0.3875
40	19.13	2.6657	0.0681	0.4225	1.2931	10.5308	0.3682
42	19.10	2.6658	0.0698	0.4263	1.2989	10.4320	0.3706
45	18.91	2.6531	0.0701	0.4218	1.2853	10.4038	0.3232
56	19.15	2.6925	0.0698	0.4264	1.2993	10.4439	0.3752
57	19.23	—	0.0701	0.4249	1.2971	—	—
61	19.19	—	0.0700	0.4266	1.2935	10.6183	0.3605
62	19.17	2.6820	—	—	—	—	—
64	19.15	2.6710	0.0671	0.4271	1.2908	10.6118	0.3272
67	19.22	2.6708	—	—	—	—	—
70	19.22	2.6975	0.0701	0.4235	1.2958	10.5477	0.3826
73	19.28	—	0.0701	0.4228	1.3052	10.5715	0.3760
75	19.18	2.6656	—	—	—	—	—
76	19.13	—	0.0710	0.4272	1.2962	10.5109	0.3731
81	19.23	2.6902	0.0701	0.4269	1.3038	10.5809	0.3682
Average	19.17_7	2.6780_5	0.0698_8	0.4254_5	1.2969_8	10.5521_7	0.3661_6

Table 3.

No.	Cl	Br	CO_3	SO_4	Ca	Mg	Na	K
31	55.38	0.19	0.20	7.76	1.23	3.74	30.42	1.09
32	55.28	0.19	0.20	7.73	1.23	3.73	30.59	1.06
36	55.33	0.19	0.20	7.71	1.23	3.74	30.54	1.06
38	55.38	0.19	0.20	7.75	1.23	3.76	30.38	1.12
40	55.36	0.19	0.20	7.72	1.22	3.75	30.50	1.07
42	55.44	0.19	0.20	7.75	1.24	3.78	30.33	1.08
45	55.37	0.19	0.20	7.78	1.24	3.77	30.51	0.95
56	55.44	0.19	0.20	7.81	1.24	3.77	30.28	1.09
64	55.29	0.19	0.20	7.73	1.23	3.73	30.69	0.95
70	55.35	0.19	0.20	7.78	1.22	3.74	30.42	1.10
81	55.33	0.19	0.20	7.75	1.23	3.76	30.49	1.06
Average	$55.35_9 \pm 0.03_3$	0.19	0.20	$7.75_2 \pm 0.02_2$	$1.23_1 \pm 0.00_5$	$3.75_2 \pm 0.01_5$	$30.46_8 \pm 0.09_3$	$1.05_7 \pm 0.03_7$

The Comparison of Compositions between the World's Average and the Western Pacific Ocean. From these results, we can obtain the average composition of the salt of the Western Pacific, taking into consideration the content of bromine, strontium and boric acid. In Table 4, the total salt composition of the Western Pacific is compared with those of the world's mean. For the average composition of the world, the values

calculated by T. G. Thompson[6] and by H. Wattenberg[7] have been adopted, and also the analyses of W. Dittmar[8] have been used as a reference. As seen from this table, the differences in the compositions between the world's average and the Western Pacific are very small, except that the values of sodium and potassium are a little lower, while on the contrary those of chloride and magnesium are but slightly higher, than the world's average. This tendency will become much clearer, when the amount of each component is represented as the number of mols per kilogram of water, assuming that the chlorinities are the same. In Table 5 the number of each element has been calculated when the chlorinity is Cl = 19.374‰

Table 4. The Percentage Compositions of the Oceanic Salt.

	Thompson	Wattenberg	Dittmar	Average	The Western Pacific
Na	30.60	30.43	30.59	30.52	30.47
Mg	3.70	3.72	3.73	3.73	3.74
Ca	1.19	1.19	1.20	1.19	1.19
Sr	0.04	0.04	—	0.04	0.04
K	1.09	1.11	1.11	1.10	1.06
Cl	55.18	55.14	55.29	55.17	55.31
SO_4	7.72	7.70	7.69	7.70	7.73
CO_3	0.30	0.40	0.21	0.30	0.20
Br	0.19	0.19	0.19	0.19	0.19
$B(OH)_3$	—	0.08	—	0.08	0.08

Table 5. The Number of Mols per kilo-gram Water. Cl = 19.374‰.

	Thompson	Wattenberg	Dittmar	Average	The Western Pacific
Na	0.4662	0.4638	0.4652	0.4651	0.4634
K	0.0098	0.0099	0.0093	0.0097	0.0095
Mg	0.0533	0.0535	0.0534	0.0534	0.0539
Ca	0.0104	0.0104	0.0105	0.0104	0.0104
Sr	—	0.00015	—	0.00015	0.00017
Cl	0.5454	0.5454	0.5454	0.5454	0.5454
Br	0.0008	0.00083	0.00083	0.0008	0.0008
SO_4	0.0281	0.0281	0.0280	0.0281	0.0282
CO_3	0.0017	0.0023	0.0012	0.0017	0.0012
$B(OH)_3$	0.00045	0.00045	—	0.00045	0.00043

In according with the custom of oceanography, the ratio of the number of the promilles of each element to the chlorinity has been calculated and compared in a like manner with the world's average (Table 6). Since the ratio of the chlorinity to the salinity is almost constant, the result of the comparison is naturally the same as that of Table 5.

(6) T.G. Thompson, "Bulletin of the National Research Council, No. 85, Physics of the Earth. V. Oceanography," 69, New York (1932).

(7) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236** (1938), 339.

(8) H.W. Harvey, "The Chemistry and Physics of Sea Water," 36, Camgridge (1928).

Table 6.

	Thompson	Wattenberg	Dittmar	Average	The Western Pacific
Na	0.55342	0.55105	0.55326	0.55258	0.54974±0.001975
K	0.01971	0.02000	0.02007	0.01993	0.01909±0.000620
Mg	0.06697	0.06746	0.06728	0.06719	0.06736±0.000192
Ca	0.02152	0.02157	0.02170	0.02159	0.02155±0.000067
SO_4	0.13962	0.13947	0.13908	0.13939	0.13967±0.000375

A Comparison between the Western Pacific and the Northeastern Pacific. It is interesting to compare the salt compositions of the western and the northeastern parts of the Pacific Ocean. T. G. Thompson and his collaborators[9] have determined very precisely the salt compositions of the opposite side of the Pacific Ocean. The comparison of the chlorinity ratios on both sides of the ocean is shown in Table 7. It is quite noteworthy that there is an astonishing agreement between the analytical results of the west and the northeast. This agreement is by no means accidental, because the mean deviation of the analytical results are very small as shown in Table 3.

In spite of this good unity, however, we have to acknowledge the small, but significant discrepancy in the ratios of magnesium to the chlorinity. It will be investigated in the near future whether this discrepancy is substantial or not.

Table 7. A Comparison of Chlorinity Ratios of Elements in the Northeastern and the Western Pacific Ocean.

	Northeast	West
Na	0.5495	0.5497
K	0.0191	0.0191
Mg	0.0669	0.0676
Ca	0.02150	0.02155
SO_4	0.1396	0.1397

Summary.

(1) The major constituents of sea water from the Western Pacific Ocean near Japan have been quantitatively determined. The analytical results are as follows: the difference in the compositions between the world's average and the Western Pacific is very small, except that the values of sodium and potassium are a little lower, while those of chloride and magnesium are but slightly higher, in the latter than in the former.

(2) It is quite noteworthy that there is an astonishing agreement between the analytical results of the west and the northeast side of the Pacific Ocean.

(9) *Loc. cit.*, p. 94-203.

(3) A new indicator has been used for the determination of chlorinity; that is a mixed solution of fluorescein and starch. The superiority of this indicator has been briefly discussed.

In conclusion, the author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his earnest assistance throughout this work.

The Central Meteorological Observatory of Japan, Tokyo,

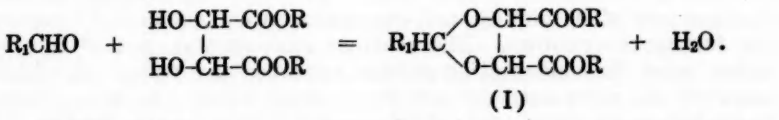
Synthesis of Cyclic Derivatives of Tartaric Acid by Condensing Alkyl *d*-Tartrates with Aromatic Aldehydes. (Optical Activity and Chemical Structure in Tartaric Acid. VI.*)

By Yojiro TSUZUKI.

(Received January 10, 1939.)

In a paper of a series of synthetic studies on the cyclic derivatives of tartaric acid, the author has noticed that a substituent exerts a certain remarkable effect due to the position on the optical activity of the compound, and has pointed out that this effect is closely related with the phenomena of light-absorption, so that it must be considered as a definitely electronic effect.(1)

The purpose of the present work is to prepare cyclic compounds of similar structure by condensing alkyl *d*-tartrates with various aromatic aldehydes, in order to investigate the electronic effect of a substituent on optical activity by observing how the position and the chemical nature of a substituent in the aromatic nucleus of the resulting compounds affect the optical activity.



(I)

The condensation of tartaric acid and its esters with benzaldehyde has already been reported by several authors, and the products were used for the study of the optical activity of tartaric acid, since they are strongly

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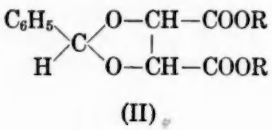
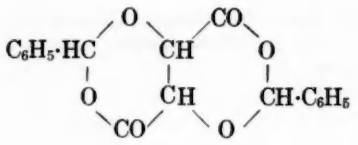
* Paper V: this Bulletin, **14** (1939), 19.

(1) Y. Tsuzuki, this Bulletin, **12** (1937), 487.

lævo-rotatory and their behaviours with respect to the optical activity are simple. Thus B. Jones[2] obtained methyl and ethyl benzylidene-tartrates (II, R = CH_3 and C_2H_5) by condensing respective tartaric esters with benzaldehyde by means of phosphorus pentoxide as dehydrating agent, and showed that their rotatory dispersions are simple. Dibenzylidene-tartrate (III) was obtained by van Ekenstein and Blanksma[3] and its rotatory dispersion was shown by Austin[4] to be also simple. Various derivatives of this compound were prepared by J. W. Pette[5] from tartaric acid and aldehydes by the action of phosphorus pentoxide.



(II)



(III)

The author has carried out the condensations of ethyl *d*-tartrate with *o*-, *m*- and *p*-nitrobenzaldehydes, *o*- and *m*-hydroxybenzaldehydes, *p*-methoxybenzaldehyde, *o*-, *m*- and *p*-chlorobenzaldehydes, piperonal, and with cinnamic aldehyde, and further the condensation of benzaldehyde with propyl, butyl and benzyl *d*-tartrates. Phosphorus pentoxide was always used as the condensing agent with great advantage.

The general method of preparation is analogous to that of the former cases, but the temperature of the reaction must be suitably regulated according to the stability of the aldehyde. In the cases of chlorobenzaldehydes, the temperature is the highest, while in the cases of hydroxybenzaldehydes it is far lower and in the case of cinnamic aldehyde it is the lowest.

Many of the condensation products are solids of low melting points. The optical rotatory power was observed in ethyl alcohol, benzene, and cyclohexane. The magnitudes of their optical activities are found various. Some of them are strongly negative, while some others less negative, and even positive. Discussion will be made on this subject in the next paper.

Ethyl *o*-Nitrobenzylidene-*d*-tartrate (I, R_1 = *o*-NO_2·C_6H_4, R = C_2H_5). To a solution of 7 g. *o*-nitrobenzaldehyde (Kahlbaum) and 10 g. ethyl *d*-tartrate was added 7 g. phosphorus pentoxide in portions at 80–100° in the course of 40 minutes, and the mixture was kept at this temperature for further 15 minutes. The reaction mixture was poured into 50 c.c. water, when the condensation product appeared as a yellow oil, which was solidified on repeatedly rubbing it in fresh water. It was purified by recrystallisation from 80% ethyl alcohol. Pale yellow needles. Yield

(2) B. Jones, *J. Chem. Soc.*, **1933**, 788. H. O. L. Fischer and H. Appel used zinc chloride as the dehydrating agent in preparing the methyl ester, *Helv. Chim. Acta*, **17** (1934), 1581.

(3) *Rec. trav. chim.*, **25** (1906), 162.

(4) T. M. Lowry, "Optical Rotatory Power," 290, London (1935).

(5) J. W. Pette, *Rec. trav. chim.*, **53** (1934), 967.

2.3 g. Melting point 60°. $[\alpha]_D^{20}$ +40.3°, $[M]_D^{20}$ +136.7° (in ethyl alcohol, 3.618%). $[\alpha]_D^{20}$ +34.3°, $[M]_D^{20}$ +116.3° (in benzene, 4.864%). $[\alpha]_D^{20}$ +6.9°, $[M]_D^{20}$ +23.4° (in cyclohexane, 0.6726%). Found: N, 4.21. Calc. for $C_{15}H_{17}NO_8$ (339.14): N, 4.13%.

Ethyl *m*-Nitrobenzylidene-*d*-tartrate. To a mixture of 5 g. *m*-nitrobenzaldehyde (Kahlbaum) and 7 g. ethyl *d*-tartrate was added 8 g. phosphorus pentoxide in portions at 115–125° in the course of 40 minutes and the heating of the mixture was continued at that temperature for 30 minutes. The brown liquid was poured into cold water. The separating brown oil was solidified by repeatedly rubbing in cold water. It was purified by recrystallising four times from absolute alcohol. Pale yellow needles. Melting point 43.5–44°. Yield 3 g. $[\alpha]_D^{20}$ −35.65°, $[M]_D^{20}$ −120.9° (in alcohol, 3.295%). $[\alpha]_D^{20}$ −37.35°, $[M]_D^{20}$ −126.7° (in benzene, 7.638%). $[\alpha]_D^{20}$ −26.1°, $[M]_D^{20}$ −88.3° (in cyclohexane, 1%). Found: N, 4.37. Calc. for $C_{15}H_{17}NO_8$ (339.14): N, 4.13%.

Ethyl *p*-Nitrobenzylidene-*d*-tartrate. Phosphorus pentoxide (8 g.) was added in portions to a mixture of 6 g. *p*-nitrobenzaldehyde (Kahlbaum) and 8.5 g. ethyl *d*-tartrate at 100–108° in the course of 25 minutes, and heating was continued for 15 minutes. Yield 4 g. Pale yellow needles (from absolute alcohol) melting at 59–59.5°. $[\alpha]_D^{20}$ −22.2°, $[M]_D^{20}$ −75.2° (in alcohol, 2.113%). $[\alpha]_D^{20}$ −25.5°, $[M]_D^{20}$ −86.5° (in benzene, 6.136%). $[\alpha]_D^{20}$ −15.4°, $[M]_D^{20}$ −52.3° (in cyclohexane, 0.77%). Found: N, 4.27. Calc. for $C_{15}H_{17}NO_8$ (339.14): N, 4.13%.

Ethyl *o*-Hydroxybenzylidene-*d*-tartrate (I, $R_1 = o\text{-}OH\cdot C_6H_4$, $R = C_2H_5$). To a mixture of 5 g. salicylaldehyde (Takeda) and 8.5 g. ethyl *d*-tartrate was added 7 g. phosphorus pentoxide in portions at 40–50° in the course of 30 minutes. The reaction mixture was poured into cold water. The separating oil resisted solidification. Purification was done by precipitating four times from ethyl alcoholic solution with water, and washing with petroleum ether. Colourless crystals. Yield 2 g. Melting point 59° after sintering. $[\alpha]_D^{20}$ −35.8°, $[M]_D^{20}$ −111.3° (in alcohol, 1.6%). $[\alpha]_D^{20}$ −55.1°, $[M]_D^{20}$ −170.8° (in benzene, 3%). $[\alpha]_D^{20}$ −53.7°, $[M]_D^{20}$ −166° (in cyclohexane, 0.4%). Saponification equivalent: 154.4. Calc. for $C_{15}H_{18}O_7$: 155.07.

Ethyl *m*-Hydroxybenzylidene-*d*-tartrate. To a mixture of 4.7 g. *m*-hydroxybenzaldehyde (Th. Schuchardt) and 8 g. ethyl *d*-tartrate was added 8 g. phosphorus pentoxide in portions at 70–80° in the course of 30 minutes. The reaction product was poured into water, when a brown oil separated out. The oil was purified by precipitating from water–alcohol three times and finally by distilling in vacuum. Colourless crystals. Melting point 37–38.5°. Boiling point 207° (0.5 mm.). Difficultly soluble in cyclohexane. $[\alpha]_D^{20}$ −32.5°, $[M]_D^{20}$ −101° (in alcohol, 5.5%). $[\alpha]_D^{20}$ −26.1°, $[M]_D^{20}$ −80.9° (in benzene, 1.138%). Saponification equivalent: 155.1. Calc. for $C_{15}H_{18}O_7$: 155.07.

Ethyl *p*-Methoxybenzylidene-*d*-tartrate (I, $R_1 = p\text{-}CH_3O\cdot C_6H_4$, $R = C_2H_5$). To a mixture of 7 g. aubepine (Merck) and 10 g. ethyl *d*-tartrate

was added 10 g. phosphorus pentoxide at 50–60° in the course of 30 minutes and the reaction mixture was heated at 65° for one hour. The ethereal extract of the reaction product, washed repeatedly with a concentrated solution of KBO_2, dried over anhydrous sodium sulphate, and fractionated in vacuum, gave 5 g. pale yellow viscous liquid boiling at 183° (0.3 mm.). $[\alpha]_D^{20}$ −27.86°, $[M]_D^{20}$ −90.3° (in alcohol, 3.604%). $[\alpha]_D^{20}$ −26.87°, $[M]_D^{20}$ −87.09° (in benzene, 6.570%). $[\alpha]_D^{20}$ −18.3°, $[M]_D^{20}$ −59.4° (in cyclohexane, 1.364%). Saponification equivalent: 161.0. Calc. for $C_{16}H_{20}O_7$: 162.08.

Ethyl *o*-Chlorobenzylidene-*d*-tartrate (I, $R_1 = o\text{-}Cl\cdot C_6H_4$, $R = C_2H_5$). To a solution of 5.5 g. *o*-chlorobenzaldehyde (Takeda) and 8 g. ethyl *d*-tartrate was added 8 g. phosphorus pentoxide at 100–120° in the course of 40 minutes. The reaction product was poured into cold water. The separating oil, reprecipitated twice from ethyl alcohol with water, suddenly solidified to colourless crystals. Melting point 36–36.5°. Yield 6 g. $[\alpha]_D^{20}$ −15.9°, $[M]_D^{20}$ −52.2° (in alcohol, 4.164%). $[\alpha]_D^{20}$ −28.6°, $[M]_D^{20}$ −94.0° (in benzene, 8.158%). $[\alpha]_D^{20}$ −22.1°, $[M]_D^{20}$ −72.6° (in cyclohexane, 1.358%). Found: Cl, 10.41 (Piria-Schiff). Calc. for $C_{15}H_{17}O_6Cl$ (328.60): Cl, 10.79%.

Ethyl *m*-Chlorobenzylidene-*d*-tartrate. To a mixture of 3.05 g. *m*-chlorobenzaldehyde[6] and 4.50 g. ethyl *d*-tartrate was added 5 g. phosphorus pentoxide at 100° in the course of 40 minutes and the heating was continued for 20 minutes. The liquid was more easily coloured than in the case of the *o*-compound. The reaction product, poured into water, reprecipitated twice from water–alcohol, and finally fractionated in vacuum, gave 3 g. colourless crystals. Boiling point 153° (1 mm.). Melting point 29–30°. $[\alpha]_D^{20}$ −31.44°, $[M]_D^{20}$ −103.3° (in alcohol, 3.455%). $[\alpha]_D^{20}$ −30.16°, $[M]_D^{20}$ −99.10° (in benzene, 2.171%). $[\alpha]_D^{20}$ −18.47°, $[M]_D^{20}$ −60.7° (in cyclohexane, 1.3205%). Found: Cl, 10.64 (Piria-Schiff). Calc. for $C_{15}H_{17}O_6Cl$ (328.60): Cl, 10.79%.

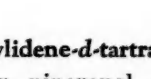
Ethyl *p*-Chlorobenzylidene-*d*-tartrate. To a mixture of 3 g. *p*-chlorobenzaldehyde[7] and 6 g. ethyl *d*-tartrate was added 5 g. phosphorus pentoxide at 110–120° in the course of 40 minutes. The phosphoric acid was coloured reddish, but the liquid only faintly yellow, and the heating was continued for further 30 minutes. The reaction product was extracted with ether. The ethereal solution, shaken thrice with concentrated KBO_2, dried over sodium sulphate, and fractionated in vacuum, gave a viscous pale yellowish liquid (4 g.) boiling at 180° (0.5 mm.). $[\alpha]_D^{20}$ −28.1°, $[M]_D^{20}$ −92.3° (in alcohol, 1.496%). $[\alpha]_D^{20}$ −26.8°, $[M]_D^{20}$ −88.2° (in benzene, 3.955%). $[\alpha]_D^{20}$ −14.7°, $[M]_D^{20}$ −48.3° (in cyclohexane, 1.302%). Found: Cl, 10.42 (Piria-Schiff). Calc. for $C_{15}H_{17}O_6Cl$ (328.60): Cl, 10.79%.

Ethyl Cinnamylidene-*d*-tartrate (I, $R_1 = C_6H_5\cdot CH{:}CH$, $R = C_2H_5$). To a solution of 5.12 g. cinnamic aldehyde (Shuzui) and 8 g. ethyl *d*-

(6) Prepared from *m*-nitrobenzaldehyde (Kahlbaum), b.p. 105° (25 mm.), "Organic Syntheses," **13**, 28.

(7) Prepared from *p*-chlorotoluene, b.p. 98° (18 mm.), m.p. 47°, "Organic Syntheses," **12**, 12.

tartrate was added 8 g. phosphorus pentoxide in portions with gentle warming. The brownish-coloured liquid was poured into water. The separating oil was reprecipitated twice from dilute alcohol, solidified, and recrystallised from petroleum ether. Colourless crystals melting at 54.4°. Yield 1.5 g. $[\alpha]_D^{20}$ −3.70°, $[M]_D^{20}$ −11.9° (in alcohol, 4.046%). $[\alpha]_D^{20}$ −21.0°, $[M]_D^{20}$ −67.3° (in benzene, 4.348%). $[\alpha]_D^{20}$ +12.5°, $[M]_D^{20}$ +40° (in cyclohexane, 0.697%). Saponification equivalent: 161.8. Calc. for $C_{17}H_{20}O_6$: 160.08.

Ethyl 3,4-Methylenedioxybenzylidene-*d*-tartrate (I, $R_1 =$  , $R = C_2H_5$). To a mixture of 5.1 g. piperonal (Merck) and 7 g. ethyl *d*-tartrate was added 6 g. phosphorus pentoxide in portions at 60° in the course of 30 minutes. The deeply coloured liquid was poured into water and repeatedly rubbed in water. The solidified product was recrystallised from ethyl alcohol four times. Colourless silky needles. Yield 1 g. Melting point 40.5–41.5°. $[\alpha]_D^{18}$ −32.6°, $[M]_D^{18}$ −110° (in alcohol, 2.715%). $[\alpha]_D^{18}$ −31.0°, $[M]_D^{18}$ −105° (in benzene, 4.010%). $[\alpha]_D^{20}$ −18.9°, $[M]_D^{20}$ −63.8° (in cyclohexane, 0.958%). Saponification equivalent: 169.6. Calc. for $C_{16}H_{18}O_8$: 169.07.

Propyl Benzylidene-*d*-tartrate (I, $R_1 = C_6H_5$, $R = C_3H_7$). To a solution of dipropyl *d*-tartrate (16 g.) and freshly distilled benzaldehyde (15 g.) was added 15 g. phosphorus pentoxide in portions at 60–70°. The liquid was coloured deeply brown. The product was extracted with ether. The ethereal solution was washed by shaking with KBO_2 solution five times. After evaporating off ether and benzaldehyde, the residue was fractionated in vacuum. This process of purification was once repeated. Colourless liquid boiling at 169° (0.3 mm.). Yield 9 g. d_4^{20} 1.1333. n_D^{20} 1.4882, M_D 81.93 (81.50). $[\alpha]_D^{20}$ −35.87°, $[M]_D^{20}$ −115.6° (homog.). Found: C, 63.50; H, 6.96. Calc. for $C_{17}H_{22}O_6$ (322.18): C, 63.32; H, 6.88%.

Butyl Benzylidene-*d*-tartrate (I, $R_1 = C_6H_5$, $R = C_4H_9$). To a solution of dibutyl *d*-tartrate (15 g.) and freshly distilled benzaldehyde (8 g.) was added 10 g. phosphorus pentoxide in portions at 60° in the course of 30 minutes, and thereafter heated at 60–70° further for 30 minutes. The liquid mixture was deeply coloured. The ethereal extract was shaken with N/2 KBO_2 four times and once with water, and dried over sodium sulphate. After evaporating off ether, the residue was fractionally distilled. Almost colourless liquid. Yield 9 g. Purification is effected by shaking the ethereal solution with N/2 KBO_2 several times, drying over sodium sulphate, and by fractional distillation in vacuum. This process was once repeated. Colourless liquid. Boiling point 189–190° (0.2 mm.). d_4^{20} 1.1004, d_4^{25} 1.0974. n_D^{25} 1.4830, M_D 91.14 (90.74). $[\alpha]_D^{20}$ −31.22°, $[M]_D^{20}$ −109.3° (homog.). Found: C, 65.08; H, 7.24. Calc. for $C_{19}H_{26}O_6$ (350.21): C, 65.10; H, 7.48%.

Benzyl Benzylidene-*d*-tartrate (I, $R_1 = C_6H_5$, $R = C_6H_5{\cdot}CH_2$). To a mixture of benzyl *d*-tartrate (10 g.) and freshly distilled benzaldehyde

(3.22 g.) was added 7 g. phosphorus pentoxide in portions at 70° in the course of 60 minutes. The resulted fatty mass was poured into water, and the separating solid was recrystallised from absolute alcohol three times. White crystals. Yield 4 g. Melting point 86°. $[\alpha]_D^{20}$ −39.7°, $[M]_D^{20}$ −166° (in alcohol, 1.356%). $[\alpha]_D^{20}$ −39.38°, $[M]_D^{20}$ −164.8° (in benzene, 12.18%). Found: C, 71.64; H, 5.30. Calc. for $C_{25}H_{22}O_6$ (418.18): C, 71.74; H, 5.30%.

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Austauschreaktion der Wasserstoffatome zwischen Nitrophenol und Wasser. III. Aktivierungsenergie.[1]

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Inhaltsübersicht. Die Austauschreaktion der Kernwasserstoffatome des *m*- und *p*-Nitrophenols in alkalischer Lösung wird bei verschiedenen Temperaturen zwischen 100° und 139°C. untersucht. Die dabei gefundenen Werte der (scheinbaren) mittleren Geschwindigkeitskonstante $\bar{k}$ in 1 N KOH-Lösung kann durch die Ausdrücke wiedergegeben werden:

$$\log \bar{k}(\text{meta}) = (9.3 \pm 0.7) - \frac{29{,}000 \pm 1{,}200}{4.574\ T} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1},$$

$$\log \bar{k}(\text{para}) = (9.0 \pm 0.6) - \frac{28{,}400 \pm 1{,}000}{4.574\ T} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1}.$$

Für *p*-Nitrophenol gilt fast dieselbe Aktivierungsenergie wie in 1 N KOH-Lösung auch in 3 N KOH-Lösung. Rechnet man die oben angegebene direkt experimentell gefundene (scheinbare) Geschwindigkeitskonstante $\bar{k}$ in die (wahre) Geschwindigkeitskonstante $\bar{k}_0$ für die grundlegende Reaktion zwischen Phenolationen und neutralen Phenolmolekülen um, dann wird sie durch die Ausdrücke wiedergegeben:

$$\bar{k}_0(\text{meta}) = 10^{11.3}\ e^{-\frac{29{,}000}{RT}} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1},$$

$$\bar{k}_0(\text{para}) = 10^{11.0}\ e^{-\frac{28{,}400}{RT}} \quad (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1}.$$

Die so gefundenen Werte der Aktivierungsenergie für die Nitrophenole werden mit dem früher gefundenen Wert (24,800 cal.) für das unsubstituierte Phenol verglichen und der Einfluss der Nitrogruppe auf die Austauschreaktion der Kernwasserstoffatome wird diskutiert.

Einleitung. Wir kamen beim letzten Versuch (vgl. II. Mittl.) zu dem Schluss, dass die Austauschreaktion der Kernwasserstoffatome des Nitrophenols in alkalischer Lösung hauptsächlich zwischen Phenolationen

(1) I. Mittl.: dies Bulletin, **13** (1938), 318; II. Mittl.: *ibid.*, **13** (1938), 595 und 631.

und neutralen Phenolmolekülen stattfindet, wie das folgende Schema zeigt:

$$C_6H_4NO_2O^- + C_6H_4NO_2OD = C_6H_3DNO_2O^- + C_6H_4NO_2OH \qquad (1).$$

Daranschliessend untersuchten wir mit Hilfe derselben Versuchsmethode wie beim Nitrophenol die Austauschreaktion des unsubstituierten Phenols in alkalischer Lösung und kamen zu dem Ergebnis, dass die mittlere Geschwindigkeitskonstante $\bar{k}_0$ für die der Reaktion (1) entsprechende grundlegende Reaktion zwischen unsubstituierten Phenolationen und neutralen Phenolmolekülen durch den Ausdruck (2) richtig wiedergegeben werden kann:[2]

$$\bar{k}_0(\text{Phenol}) = 10^{10.8}\, e^{-\frac{24,800}{RT}}\ (\text{Mol/Liter})^{-1}(\text{Sek.})^{-1} \qquad (2).$$

Es liegt deshalb nahe, die Aktivierungsenergie der Reaktion (1) für die isomerischen Arten der Nitrophenole zu bestimmen und diese mit dem früher bestimmten Wert für das unsubstituierte Phenol zu vergleichen.

Versuch. Aus dem oben erwähnten Grund wird zunächst das Austauschäquivalent na des *m*- und *p*-Nitrophenols[3] in der mit KOH versetzten Lösung mit Hilfe genau derselben Versuchsmethode, wie die in II. Mittl. beschrieben wurde, bei verschiedenen Temperaturen und verschiedenen Versuchsdauern bestimmt. Die dabei benutzte Versuchstemperatur ist 100°, 110° (bzw. 111°), 131° und 139°C. und die (analytische) Konzentration von KOH beträgt beim *m*-Nitrophenol 1 N. Dagegen werden beim *p*-Nitrophenol zwei verschiedene Stärkegrade der Lösung benutzt, nämlich 1 N und 3 N. Unter Verwendung der auf diese Weise bei verschiedenen Versuchsdauern bestimmten Werte des Austauschäquivalents na wird die Quantität $(-X \log Y)$ mit Hilfe der Gl.(3) berechnet (vgl. Gl.(16) in I. Mittl.):

$$X = \frac{V}{(n_2 M_{ph} + \frac{a_1}{a_2} M_{ph} + \frac{2}{a_2} M_w)},$$

$$Y = \frac{1 - \frac{na - n_1 a_1}{n_2 a_2}}{1 + \frac{na - n_1 a_1}{\frac{2M_w}{M_{ph}} + n_1 a_1}} \qquad (3).$$

In diesen Gl. bedeutet V das Volumen der Lösung, M_{ph} und M_w resp. die Molzahl des zum Versuch benutzten Nitrophenols und des schweren Wassers, a_1 den Verteilungsquotient des Hydroxylwasserstoffs, a_2 den des Kernwasserstoffs, n_1 die Anzahl der Hydroxylwasserstoffatome und n_2 die der (in der „zweiten" Stufe der Reaktion) austauschbaren Kern-

(2) M. Koizumi und T. Titani, dies Bulletin, **13** (1938), 681.

(3) *o*-Nitrophenol wurde nicht untersucht, weil es bei allen untersuchten Temperaturen im Wasser nicht genügend leicht löslich ist.

wasserstoffatome in einem Nitrophenolmolekül. Deshalb wird bei der praktischen Durchführung der Berechnung $a_1 = 1.08$, $a_2 = 0.90$, $n_1 = 1$, $n_2 = 2$ für *p*- und 3 für *m*-Nitrophenol gesetzt und V mit Hilfe des in Tabelle 1 in II. Mittl. angegebenen spezifischen Volumens der Lösung rechnerisch ermittelt. Die mittlere Geschwindigkeitskonstante $\bar{k}$ der Austauschreaktion der Kernwasserstoffatome bei der betreffenden Temperatur wird dann gemäss der folgenden Beziehung (4) zwischen der Quantität $(-X \log Y)$ und der Versuchsdauer t graphisch bestimmt (vgl. Gl.(15) in I. Mittl.):

$$-X \log Y = \frac{\bar{k}}{2.303} t \qquad (4).$$

Die so gewonnenen Versuchsergebnisse sind in Tabellen 1 bis 3 zusammengestellt.

Tabelle 1. *m*-Nitrophenol in 1 N KOH-Lösung.

Versuchstemp. °C.	Versuchsdauer in Stdn.	M_{ph}	M_w	n_x	$-X \log Y$	$\bar{k}/2.303$
100	50	0.0219	0.0617	1.45	0.00139	0.0000323
	150	0.0217	0.0550	2.34	0.00562	
	260	0.0208	0.0549	2.66	0.00748	
110	3	0.0216	0.0556	1.93	0.00035	0.000066 ~0.000080
	80	0.0218	0.0557	2.47	0.00636	
	150	0.0217	0.0556	2.95	0.00982	
131	3	0.0218	0.0552	1.68	0.00242	0.00063 ~0.00068
	5	0.0215	0.0561	1.90	0.00347	
	8	0.0221	0.0554	2.22	0.00511	
139	2	0.0220	0.0540	1.89	0.00352	0.00095 ~0.00105
	5	0.0216	0.0559	2.30	0.00558	
	9	0.0218	0.0548	2.70	0.00820	

Tabelle. 2. *p*-Nitrophenol in 1 N KOH-Lösung.

Versuchstemp. °C.	Versuchsdauer in Stdn.	M_{ph}	M_w	n_x	$-X \log Y$	$\bar{k}/2.303$
100	2	0.0411	0.114	1.16	0.00046	0.000030 ~0.000037
	50	0.0216	0.0555	1.31	0.00138	
	150	0.0222	0.0553	1.96	0.00617	
	260	0.0188	0.0850	2.52	0.00763	
110	30	0.0219	0.0557	1.52	0.00276	0.000087
	80	0.0222	0.0559	2.06	0.00723	
	147	0.0219	0.0540	2.46	0.0127	
131	3	0.0220	0.0551	1.43	0.00213	0.00051 ~0.00055
	5	0.0216	0.0559	1.49	0.00251	
	8	0.0218	0.0551	1.74	0.00440	
	9.5	0.0215	0.0551	1.80	0.00486	
139	2	0.0216	0.0548	1.64	0.00363	0.00117 ~0.00130
	4	0.0216	0.0558	1.78	0.00467	
	7	0.0216	0.0558	2.15	0.00828	

Tabelle 3. *p*-Nitrophenol in 2.93 N KOH-Lösung.

Versuchstemp. °C.	Versuchsdauer in Stdn.	M_{ph}	M_w	n_x	$-X \log Y$	$\bar{k}/2.303$
100	2	0.0216	0.0532	1.28	0.00114	0.000095
	50	0.0216	0.0549	1.83	0.00497	~0.000110
	100	0.0216	0.0555	2.36	0.0109	
111	10	0.0216	0.0553	1.41	0.00194	0.00024
	20	0.0216	0.0553	1.86	0.00524	~0.00026
	43	0.0216	0.0552	2.32	0.0112	
130	3	0.0216	0.0552	1.77	0.00458	0.00128
	5	0.0216	0.0553	2.08	0.0746	~0.00140
	8	0.0216	0.0554	2.27	0.098	
139	1	0.0216	0.0551	1.71	0.0415	0.0030
	3	0.0216	0.0552	2.18	0.0894	~0.0033

Unter Benutzung der in diesen Tabellen 1 bis 3 angegebenen Daten können wir nun die Aktivierungsenergie der Reaktion auf die übliche Weise ohne weiteres bestimmen, indem wir $\log(\bar{k}/2.303)$ gegen das Reziproke der absoluten Temperatur $1/T$ einzeichnen. Die dadurch gewonnenen geraden Linien in Abb. 1 und 2 können wir aber durch die Ausdrücke gut wiedergeben:

$$\log(\bar{k}/2.303)\,(\text{meta, 1 N}) = (12.5 \pm 0.7) - \frac{29{,}000 \pm 1{,}200}{4.574\,T}\,(\text{Mol/Liter})^{-1}(\text{Stunde})^{-1},$$

$$\log(\bar{k}/2.303)\,(\text{para, 1 N}) = (12.2 \pm 0.6) - \frac{28{,}400 \pm 1{,}000}{4.574\,T} \quad ,, \quad ,,$$

$$\log(\bar{k}/2.303)\,(\text{para, 3 N}) = (12.4 \pm 0.6) - \frac{28{,}000 \pm 1{,}000}{4.574\,T} \quad ,, \quad ,, \quad (5).$$

Diese Konstante $\bar{k}$ entspricht aber, wie aus der Ableitung der Gl. (3) und (4) ohne weiteres klar ist (vgl. dazu II. Mittl.), der stöchiometrischen Gl. (6):

$$C_6H_4NO_2OH + HDO = C_6H_2DNO_2OH + H_2O \qquad (6).$$

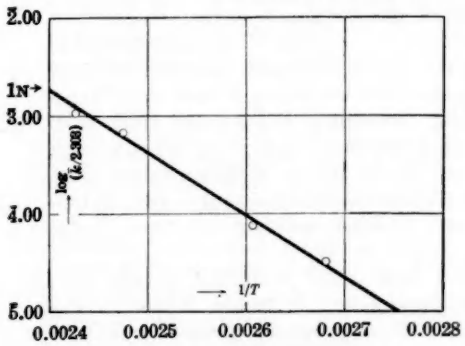


Abb. 1. *m*-Nitrophenol.

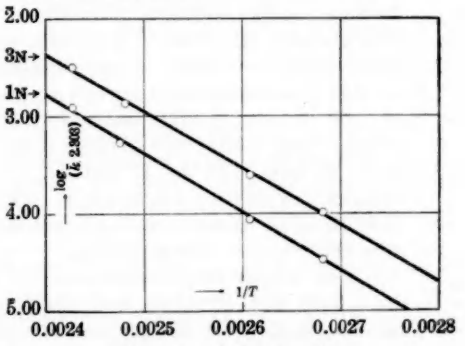


Abb. 2. *p*-Nitrophenol.

Dagegen verläuft die wirkliche Reaktion, wie darauf schon in II. Mittl. hingewiesen wurde, hauptsächlich zwischen Phenolationen und neutralen Phenolmolekülen gemäss der schon oben angegebenen Gl.(1). Wenn wir deshalb unter passenden Voraussetzungen die oben angegebene stöchiometrische Geschwindigkeitskonstante $\bar{k}$ (5) für die Reaktion (6) in die wahre Geschwindigkeitskonstante $\bar{k}_0$ für die Reaktion (1) umrechnen, dann ergeben sich die Gln. ($\bar{k}_0 = k_6$ in Gl. (18), II. Mittl.):

$$\bar{k}_0(\text{meta, 1 N}) = 10^{11.3\pm0.7} \exp\left(-\frac{29{,}000 \pm 1{,}200}{RT}\right) \text{(Mol/Liter)}^{-1}\text{(Sekunde)}^{-1},$$

$$\bar{k}_0(\text{para, 1 N}) = 10^{11.0\pm0.6} \exp\left(-\frac{28{,}400 \pm 1{,}000}{RT}\right) \text{(Mol/Liter)}^{-1}\text{(Sekunde)}^{-1},$$

$$\bar{k}_0(\text{para, 3 N}) = 10^{10.8\pm0.6} \exp\left(-\frac{28{,}000 \pm 1{,}000}{RT}\right) \text{(Mol/Liter)}^{-1}\text{(Sekunde)}^{-1} \quad (7).$$

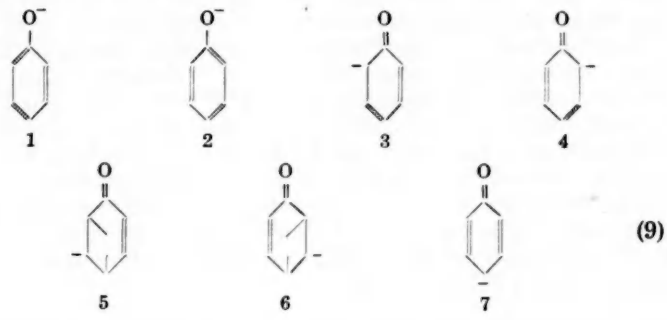
Diskussion. Aus diesen letzten Gl.(7) ersehen wir, dass der Stossfaktor sowie die Aktivierungsenergie der Reaktion für die beiden isomerischen Arten des Nitrophenols innerhalb des Messfehlerbereichs ganz übereinstimmt und weiter die grundlegende Reaktion (1) ebenso wie beim unsubstituierten Phenol als die normal verlaufende bimolekulare Reaktion aufgefasst werden kann. Für das unsubstituierte Phenol erhielten wir beim letzten Versuch[2] den Ausdruck für seine (wahre) Geschwindigkeitskonstante:

$$\bar{k}_0(\text{Phenol}) = 10^{10.8} \exp\left(-\frac{24{,}800}{RT}\right) \quad (8).$$

Die Aktivierungsenergie für *m*- und *p*-Nitrophenol ist deshalb um etwa 4 Kcal. grösser als die für das unsubstituierte Phenol. Den Grund für diesen ziemlich beträchtlichen Unterschied der Aktivierungsenergie hat man offenbar im Einfluss der im Benzolkern eingeführten Nitrogruppe zu suchen. Nach der gewöhnlichen elektrophilen Substitutionsregel wirkt die Hydroxylgruppe fördernd, dagegen die Nitrogruppe störend auf die Substitutionsreaktion der Kernwasserstoffatome, die sich der Hydroxyl- bzw. Nitrogruppe gegenüber in *o*- und *p*-Stellung befinden. Wenn wir deshalb einfacherweise annehmen, dass diese beiden entgegengesetzten Effekte der Hydroxyl- und Nitrogruppe in einem Nitrophenolmolekül bloss additiv wirken, dann müsste das *m*-Nitrophenol viel schwieriger als das *p*-Nitrophenol reagieren, ohne dass der störende Effekt der Nitrogruppe unvergleichbar geringer als der fördernde Effekt der Hydroxylgruppe sein sollte, wie darauf schon in I. Mittl. hingewiesen wurde (vgl. dazu Formel (3) in I. Mittl.). Aber diese letzte Voraussetzung entspricht der Wirklichkeit nicht, weil die Aktivierungsenergie für Nitrophenole sich in der vorliegenden Arbeit deutlich grösser als die für das unsubstituierte Phenol erwies.

Die Experimentalresultate weisen aber ohne weiteres darauf hin, dass man das Problem am zweckmässigsten auf folgende Weise zu behandeln hat. Wir ziehen nämlich zunächst nur den dirigierenden Effekt der Hydroxylgruppe auf die Kernaustauschreaktion in Betracht und dann

den Effekt der Nitrogruppe als die (kleine) Störung auf diesen massgebenden Effekt der Hydroxylgruppe in Rechnung. Nun wird als die Hauptsache für den dirigierenden Effekt der Hydroxylgruppe im allgemeinen die Mesomerie des Phenolmoleküls bzw. -ions angenommen.[4] Gemäss dieser Annahme kommen bei der Austauschreaktion der Kernwasserstoffatome des Phenols die folgenden sieben mesomerischen Formen in Betracht:[5]



(9)

Unter diesen sieben Formen müssen beim gewöhnlichen unsubstituierten Phenol die *o*- und *p*-Chinoidformen, nämlich die Formen 3, 4 und 7, den *m*-Chinoidformen 5 und 6 gegenüber überwiegend grösseres statistisches Gewicht besitzen,[6] weil der wirkliche Austausch hauptsächlich an der *o*- und *p*-Stellung stattfindet. Diese Sachlage erfährt aber beim Nitrophenol durch die Einführung der Nitrogruppe eine gewisse Störung.

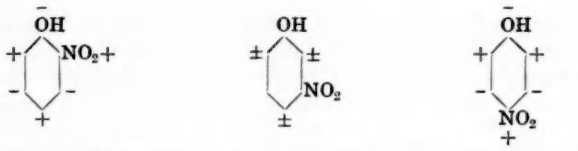
Wird nämlich irgendein Kernwasserstoffatom, das sich der Hydroxylgruppe gegenüber in *o*-, *m*- bzw. *p*-Stellung befindet, durch die Nitrogruppe substituiert, dann werden die Elektronen (bzw. Elektronenwolke) im ganzen Molekül durch den „induktiven Effekt" dieser Gruppe nach ihrer Stellung mehr oder weniger angezogen bzw. angehäuft. Durch diese Elektronenverschiebung wird aber die Elektronendichte an den anderen Stellen im Phenolmolekül und folglich auch die Austauschwahrscheinlichkeit an diesen betreffenden Stellen vermindert. Wenn z.B. das eine in *m*-Stellung befindliche H-Atom durch die Nitrogruppe substituiert wird, dann werden die Elektronen, die bisher hauptsächlich (bis auf die an der Hydroxylgruppe) an der *o*- und *p*-Stellung angehäuft waren, mehr oder weniger nach der *m*-Stellung angezogen und dadurch die Austauschreak-

(4) Vgl. dazu K.H. Gieb, *Z. physik. Chem.*, A, **180** (1937), 211.

(5) Bei dieser Bezeichnung haben wir statt des neutralen Phenolmoleküls das Phenolation in Rechnung gezogen, weil die wirkliche Austauschreaktion zwischen Phenolationen und neutralen (schweren) Phenolmolekülen stattfindet. Wir haben weiter die mesomerischen Formeln nach dem Prinzip des „ersten" Nährungsverfahrens aufgezeichnet. Deshalb sehen die *m*-Chinoidformen im Vergleich mit den anderen Formen etwas eigentümlich aus. Diese Eigentümlichkeit können wir aber umgehen, wenn wir uns des „zweiten" Nährungsverfahrens bedienen (vgl. dazu W. Hückel, *Z. Elektrochem.*, **43** (1937), 752 und 827).

(6) In jedem Fall besitzen natürlich die Benzenoidformen 1 und 2 im Vergleich mit den anderen Formen immer unvergleichbar grösseres statistisches Gewicht. Bei der vorliegenden Diskussion soll der Vergleich nur zwischen den verschiedenen Chinoidformen ausgeführt werden.

tion an der *o*- und *p*-Stellung erschwert. Auf ähnliche Weise können wir auch die Schwierigkeit, mit der die Austauschreaktion des *p*-Nitrophenols stattfindet, erklären. Doch weil in diesem Fall die Elektronen schon von vorn herein, d.h. beim unsubstituierten Phenol, an der *p*-Stellung ziemlich deutlich angehäuft sind (vgl. oben), haben wir den störenden Effekt der Nitrogruppe lieber auf dem folgenden Wege mittelbar in Rechnung zu ziehen. Wird nämlich die Nitrogruppe in *p*-Stellung des Phenolmoleküls eingeführt, dann wird das statistische Gewicht der *p*-Chinoidform in höherem Masse als bisher vergrössert, und zwar dadurch, dass die Elektronen hauptsächlich von der Hydroxylgruppe nach der in *p*-Stellung befindlichen Nitrogruppe angezogen werden. Dadurch wird aber das statistische Gewicht der Benzenoidformen 1 und 2 und folglich weiter das der sich mit diesen im Gleichgewicht befindlichen *o*-Chinoidformen 3 und 4 verringert. Den störenden Effekt der in *p*-Stellung eingeführten Nitrogruppe können wir deshalb dem oben angegebenen unmittelbar störenden Effekt der in *m*-Stellung eingeführten Nitrogruppe gegenüber mehr als einen mittelbaren Effekt auffassen. Alle diese Verhältnisse lassen sich zusammen mit dem *o*-Nitrophenol durch die folgenden Formeln schematisch zum Ausdruck bringen:



o-Nitrophenol *m*-Nitrophenol *p*-Nitrophenol (10).

In dieser Bezeichnung bedeutet das Pluszeichen die durch die Hydroxylgruppe bewirkte Anreicherung, dagegen das Minuszeichen die durch die Nitrogruppe bewirkte Verarmung an Elektronendichte in einer bestimmten Stelle des Benzolkerns. Beim *m*-Nitrophenol fallen nun diese beiden entgegengesetzten Effekte der Hydroxyl- und Nitrogruppe überall ganz zusammen. Deshalb wird die Leichtigkeit, mit der die Kernaustauschreaktion beim unsubstituierten Phenol stattfindet, beim *m*-Nitrophenol durch den störenden Effekt der Nitrogruppe sozusagen unmittelbar herabgesetzt. Dagegen wird beim *p*-Nitrophenol die der Hydroxylgruppe gegenüber in *o*-Stellung stattfindende Anreicherung an Elektronen durch den störenden Effekt der Nitrogruppe nicht direkt beeinflusst, weil die von dieser letzteren Gruppe herbeigeführte Verarmung an Elektronen der Hydroxylgruppe gegenüber in *m*-Stellung stattfindet. Da aber in diesem Fall, wie das Minuszeichen an der Hydroxylgruppe zeigt, die Hydroxylgruppe selbst den störenden Effekt der Nitrogruppe erleidet und dadurch die Elektronendichte an dieser Gruppe verringert wird, wird die von dieser Gruppe herrührende Anreicherung an Elektronen in *o*-Stellung auch auf mittelbarem Wege beeinflusst und zwar so, dass die Austauschreaktion an dieser Stelle erschwert wird.

Die vorliegenden Versuchsergebnisse, dass die Aktivierungsenergie für das *p*-Nitrophenol ebenso hoch wie die für *m*-Nitrophenol ist, zeigt aber, dass die Verarmung an Elektronen in den betreffenden Stellen, die

beim *p*-Nitrophenol auf mittelbarem dagegen beim *m*-Nitrophenol auf unmittelbarem Wege durch die Nitrogruppe herbeigeführt wird, in den beiden Fällen fast von derselben Grössenordnung ist. Dies ist aber nicht der Fall beim *o*-Nitrophenol, weil die Kernaustauschreaktion bei dieser Verbindung, wie beim letzten Versuch (I. Mittl.) gefunden wurde, deutlich schwieriger als bei den anderen beiden Isomeren stattfindet. Diesen Unterschied können wir jedoch mit Hilfe der schon damals hingewiesenen plausiblen Annahme ohne besondere Schwierigkeit so erklären, dass beim *o*-Nitrophenol die Wasserstoffbindung (Chelation) zwischen der benachbarten Hydroxyl- und Nitrogruppe gebildet wird. Durch diese Wechselwirkung zwischen der Hydroxyl- und Nitrogruppe werden die Elektronen ähnlich wie beim *p*-Nitrophenol von der ersteren Gruppe nach der letzteren angezogen. Aber weil diese Verschiebung der Elektronen von der Hydroxylgruppe nach der Nitrogruppe beim *o*-Nitrophenol wegen der Wasserstoffbindung in viel höherem Masse als beim *p*-Nitrophenol herbeigeführt wird, geht die Austauschreaktion der Kernwasserstoffatome im ersteren Fall viel schwieriger vor sich als im letzteren. Auf diese Weise können wir den Unterschied der Reaktionsfähigkeit der Kernwasserstoffatome zwischen dem gewöhnlichen unsubstituierten Phenol und dem Nitrophenol einerseits und zwischen den drei isomerischen Arten des Nitrophenols anderseits mindestens qualitativ befriedigend erklären.

Zum Schluss möchten wir der Nippon Gakujutsu-Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Forschungen) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung bei der Ausführung der vorliegenden Arbeit unseren wärmsten Dank aussprechen.

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The Sorption of Gases on Reduced Nickel. I. Hydrogen, Oxygen, and Hydrogen Bromide.

By Matsuji TAKEBAYASHI.

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Y. Urushibara and the present author have found that reduced nickel and reduced iron reverse the direction of the addition of hydrogen bromide to ethenoid compounds, such as allyl bromide and undecenoic acid, in the same way as oxygen.[1] As for the catalytic activity of reduced nickel

(1) This Bulletin, **11** (1936), 692, 754, 798; **12** (1937), 51, 138, 173; **13** (1938), 331, 400, 404, 574.

in these reactions it has been observed that reduced nickel that has never been in contact with air after reduction shows a much greater effect than that that has been exposed to air,[2] that the metal reduced at a temperature higher than specified for the hydrogenating catalyst is even more active than that prepared as usually,[3] and that nickel filings exhibit an activity comparable to that of reduced nickel.[4] Further, Urushibara and O. Simamura have found that isostilbene is transformed into stilbene by hydrogen bromide in the presence of either oxygen or reduced nickel.[5]

Thus some reactions other than hydrogenation have been found to be catalyzed by reduced nickel. In all these cases, however, reduced nickel is always with hydrogen bromide, reduced nickel and oxygen can take place of each other, and antioxidants, such as catechol and hydroquinone, eliminate to a greater or smaller extent the effect of reduced nickel as well as of oxygen.[6]

Further, Urushibara and Simamura,[7] studying the reaction of reduced nickel and hydrogen bromide with and without the addition of oxygen, observed that, while practically no reaction took place in the absence of oxygen, hydrogen and nickel dibromide were produced in the presence of oxygen. A balance experiment revealed that the amount of hydrogen generated was short of the equivalent to that of nickel dibromide produced, thus suggesting the formation of water; and comparative experiments with traces of water but without oxygen led to the very probable assumption that the catalyst accelerating the reaction of reduced nickel and hydrogen bromide to give hydrogen and nickel dibromide was not oxygen but the traces of water produced by the action of hydrogen bromide on nickel oxide formed from reduced nickel and oxygen. In fact, reduced nickel which had been exposed to air reacted with hydrogen bromide without added oxygen in the same way as freshly reduced nickel in the presence of oxygen. However, to exclude the possibility of the catalytic action of molecular oxygen on the reaction of hydrogen bromide and nickel, it seemed desirable to investigate the nature of the sorption of oxygen on reduced nickel.

Thus the present author has been induced to study the sorption of gases, especially hydrogen, oxygen, and hydrogen bromide, on reduced nickel. The experiments described below, however, are by no means intended for an exact investigation of the sorption itself, but have been carried out with a view to knowing the behaviours of reduced nickel toward these gaseous substances.

Apparatus, Materials, and Methods. The main part of the apparatus, as shown in Fig. 1, consists of a burette (B) for measuring the quantity of the gas sorbed, a Töpler pump (T) for pumping out the gas sorbed when

(2) Compare Exp. 7 and 8 of this Bulletin, **11** (1936), 693 with Exp. 3 of *ibid.*, **13** (1938), 401.
(3) Compare Exp. 1 and 2 of this Bulletin, **12** (1937), 53 with Exp. 3 of *ibid.*, **13** (1938), 401.
(4) This Bulletin **13** (1938), 400.
(5) *Ibid.*, **12** (1937), 507; **13** (1938), 566.
(6) *Ibid.*, **13** (1938), 400, 404, 566.
(7) *Ibid.*, **13** (1938), 407, 570.

the desorbed amount is to be measured, and a sorption tube (S) made of Terex glass and connected by means of a mercury seal.

Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at 350–400°C. Hydrogen was generated by the action of dilute sulphuric acid on zinc, and purified according to the directions of A. Klemenc.[8] Oxygen, a commercial material, was dried by passing over phosphorus pentoxide. Hydrogen bromide was prepared by the action of bromine on hot tetralin and purified according to the directions of A. Klemenc.[9]

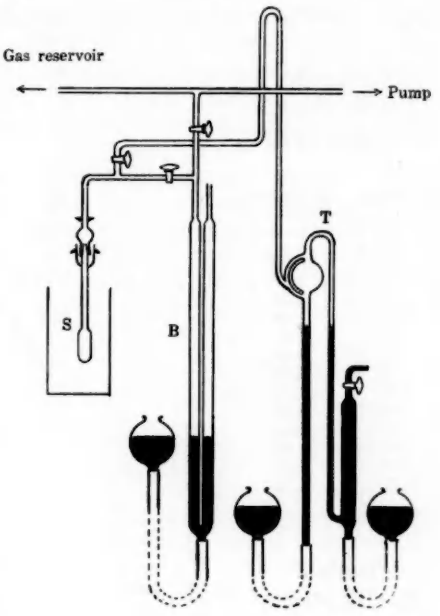

Fig. 1.

In every experiment, 1.00 g. of reduced nickel, prepared as mentioned above, was taken in the sorption tube, heated at 350°C. in the atmosphere of hydrogen for two hours to refresh the surfaces and then in vacuum for an hour to remove hydrogen, and cooled to room temperature in vacuum. Then the sorption tube containing the nickel was immersed in a thermostat; and the gas of 1 atmospheric pressure was introduced into the tube. The volume of the gas sorbed was determined by subtracting the volume of the sorption tube and the connecting tubing from the decrease of the gas in the burette. All the volumes recorded in this paper have been calculated to the normal temperature and pressure. Other particulars of the experiments are given below for respective cases.

Throughout the experiments described in this paper vacuum or evacuation was effected by a rotary pump, and pressures not exceeding 1 mm. Hg were regarded as good for the purpose.

The Sorption of Hydrogen. The sorption of hydrogen on reduced nickel has already been studied by several investigators and the activated adsorption of hydrogen on the metal has been ascertained by them.[10] The present experiments on the sorption of hydrogen were carried out

(8) A. Klemenc, "Die Behandlung und Reindarstellung von Gasen", 97, Leipzig (1938).

(9) *Loc. cit.*, (8), 196.

(10) H. Taylor and R. Burns, *J. Am. Chem. Soc.*, **43** (1921), 1273; W. Russel and H. Taylor, *J. Phys. Chem.*, **29** (1925), 1325; N. Nikitin, *Z. anorg. allgem. Chem.*, **154** (1926), 139; A. Benton and T. White, *J. Am. Chem. Soc.*, **52** (1930), 2325; S. Iijima, *Rev. Phys. Chem. Japan*, **7** (1932), 3, 24, 36; **8** (1933), 44; **12** (1938), 1.

for the purpose of comparison with those of oxygen and hydrogen bromide. The relation between time and the amount of hydrogen sorbed on 1.00 g. of reduced nickel at 20°C. was observed as shown in Tables 1 and 2. Curves I and II of Fig. 2 correspond to Tables 1 and 2 respectively.

Table 1.
The Sorption of Hydrogen at 20°C.

Time (min.)	Hydrogen sorbed (c.c.)
3/4	0.93
3	1.12
6	1.21
10	1.26
20	1 32
30	1.36
55	1.38
70	1.39
85	1.42
100	1.42
130	1.44
190	1.45
1225	1.49

Table 2.
The Sorption of Hydrogen at 20°C.

Time (min.)	Hydrogen sorbed (c.c.)
1/2	0.68
2	0.84
4	0.91
9	1.00
14	1.04
24	1.10
45	1.17
75	1.20
105	1 21

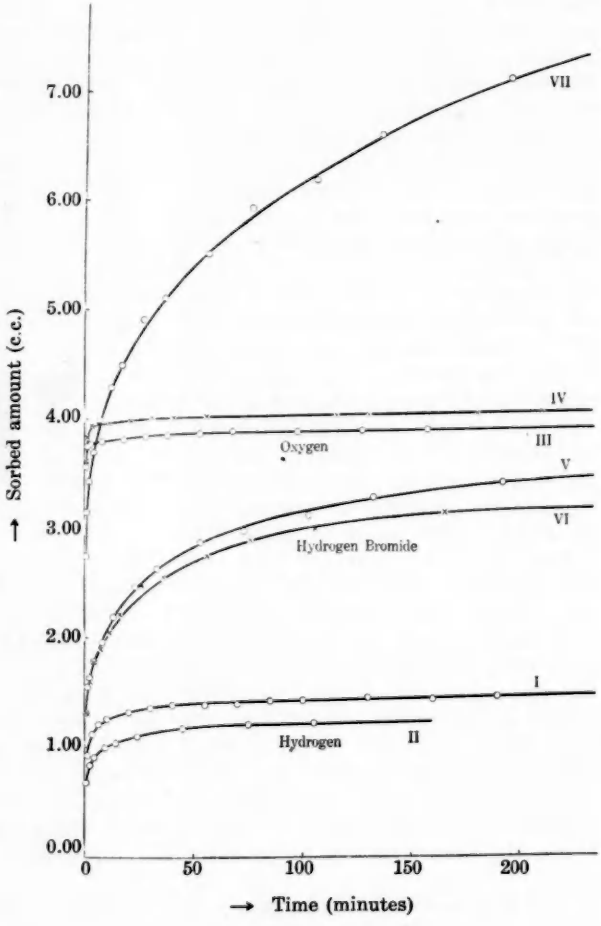

Fig. 2.

In an experiment, reduced nickel (1.00 g.) was nearly saturated with hydrogen at 20°C., when 2.21 c.c. was sorbed in 1220 minutes; then the hydrogen was evacuated for three hours; and hydrogen was again introduced at 20°C., when 0.8 c.c. was sorbed in 1245 minutes. The partial recovery of the capacity for sorption showed that at least a part of hydrogen sorbed on reduced nickel could be desorbed in three hours' evacuation.

The Sorption of Oxygen. It has been observed that reduced nickel is easily oxidized in air, and evolves heat and sometimes takes fire when it comes into contact with air.

The sorption of oxygen on freshly reduced nickel was measured at 20°C. The results are given in Tables 3 and 4 and graphically represented by Curves III and IV in Fig. 2. If compared with hydrogen, oxygen is much more rapidly and abundantly sorbed on reduced nickel. The characteristic shapes of the curves indicate that the sorption is nearly accomplished within one minute or two.

Reduced nickel (1.00 g.) was saturated with oxygen at 20°C., when 3.06 c.c. was sorbed in 1541 minutes, and then stood in vacuum for four hours at the same temperature; oxygen was again introduced at 20°C., when no more oxygen was sorbed in 1406 minutes. Thus it was shown that oxygen, once sorbed on reduced nickel, can never be desorbed in vacuum. It is very probable that the whole oxygen sorbed is bound

Table 3. The Sorption of Oxygen at 20°C.

Time (min.)	Oxygen sorbed (c.c.)
3/4	3.56
1	3.75
3	3.78
8	3.80
18	3.82
28	3.84
38	3.85
58	3.87
68	3.89
98	3.89
128	3.90
158	3.91
1440	3.94

Table 4. The Sorption of Oxygen at 20°C.

Time (min.)	Oxygen sorbed (c.c.)
3/4	3.62
1	3.84
3	3.94
6	3.95
11	3.96
21	3.98
31	4.01
41	4.01
56	4.02
116	4.02
131	4.04
181	4.05
211	4.07
1440	4.08
1566	4.09
1601	4.08
1996	4.09

chemically on nickel. Further the sorption curves (III and IV) indicate that reduced nickel is covered very quickly with a film of the oxide and hereafter oxygen can reach the metal only very slowly through the film. The rapid and abrupt sorption of oxygen on reduced nickel may be attributed partly to a transient rise of the temperature due to the evolution of heat which may favour the very quick formation of the oxide film.

An approximate calculation from the heat of formation of nickel oxide (58.08 Cal.) indicates that, when 4 c.c. of oxygen is combined with 1 g. of reduced nickel with no loss of heat, the temperature of the metal may be raised from 20°C. to above 200°C. Since it can be supposed that the higher the temperature the more oxygen would be sorbed, the oxidation of reduced nickel and the evolution of heat might be promoted reciprocally under somewhat adiabatic conditions. Thus the phenomenon observed when reduced nickel comes into contact with air is explicable.

It was then examined if the oxygen-stained surface of reduced nickel could be cleaned with hydrogen at comparatively low temperatures. Reduced nickel (1.00 g.), which had sorbed 3.75 c.c. of oxygen to saturation at 20°C. in 1370 minutes and then stood in vacuum for three hours, sorbed 2.48 c.c. of hydrogen at 20°C. in 1187 minutes. After hydrogen was evacuated at 20°C. for three hours, the reduced nickel sorbed 1.14 c.c. of oxygen at 20°C. in 1308 minutes. In a similar way, reduced nickel, which had sorbed 3.43 c.c. of oxygen to saturation at 20°C. in 2570 minutes and stood in vacuum for three hours, sorbed 8.14 c.c. of hydrogen at 96–98°C. in 330 minutes. Then the metal, after evacuation of hydrogen, sorbed 2.52 c.c. of oxygen at 20°C. in 1320 minutes. Thus the oxygen-stained nickel sorbed more hydrogen than freshly reduced nickel, and in view of the amounts of hydrogen sorbed it may be supposed that the reduction of the oxide film with hydrogen of 1 atmospheric pressure can be effected partly even at the ordinary temperature and more profoundly at 100°C. Then the consumption of oxygen by the hydrogen-treated nickel may be attributed to the partial recovery of the capacity for the sorption of oxygen rather than to the oxidation of hydrogen remaining unremoved after three hours' evacuation. In this connection it may be added that reduced nickel, which had sorbed fully hydrogen and stood in vacuum for three hours, sorbed apparently rather a smaller amount (3.10 c.c.) of oxygen than fresh nickel.

The Sorption of Hydrogen Bromide. The sorption of hydrogen bromide on freshly reduced nickel was measured at 20°C. in the dark. The results are given in Tables 5 and 6 and represented by Curves V and VI in Fig. 2. The gradual and extensive sorption suggests an activated adsorption.

Table 5. The Sorption of Hydrogen Bromide at 20°C.

Time (min.)	Hydrogen Bromide sorbed (c.c.)
1/2	1.32
1	1.55
2	1.64
4	1.79
8	1.96
13	2.19
23	2.46
33	2.63
53	2.87
73	2.97
103	3.13
133	3.28
193	3.42
253	3.57
1493	4.99

Table 6. The Sorption of Hydrogen Bromide at 20°C.

Time (min.)	Hydrogen Bromide sorbed (c.c.)
1/2	1.32
1	1.53
2	1.60
4	1.78
7	1.89
11	2.04
16	2.21
26	2.47
36	2.55
56	2.74
76	2.89
106	2.99
166	3.15
1386	4.87

Table 7. The Sorption of Hydrogen Bromide on Oxygen-stained Reduced Nickel at 20°C.

Time (min.)	Hydrogen Bromide sorbed (c.c)
1/2	2.75
1	3.15
2	3.43
4	3.70
7	3.99
12	4.29
17	4.49
27	4.91
37	5.11
57	5.52
77	5.94
107	6.20
137	6.62
197	7.15
257	7.63
317	7.98
1442	12.38
1737	22.39

Reduced nickel (1.00 g.), which had sorbed 3.45 c.c. of oxygen to saturation, consumed much more hydrogen bromide. The results are given in Table 7 and represented by Curve VII in Fig. 2. Here the possibility of the action of molecular oxygen can be readily excluded in view of the clarified nature of the sorption of oxygen on reduced nickel. As already discussed by Urushibara and Simamura[7] it is supposed that traces of water formed by the action of hydrogen bromide on nickel oxide accelerate the reaction of metallic nickel and hydrogen bromide to give hydrogen and nickel dibromide. Hence, the real amounts of hydrogen bromide withdrawn from the gaseous phase must be far greater than the values of the apparent sorption given in Table 7.

The author expresses his hearty thanks to Prof. Urushibara for his kind guidance and to Dr. I. Sano for valuable advices. Thanks are also due to Nippon Gakujutsu Shinko Kwai (Japan Society for the Promotion of Scientific Research) and to Oji Seishi Co. for grants.

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